AD 600971

FINAL REPORT

FOR

STUDY OF LOW MELT BRAZING ALLOYS

TECHNICAL DOCUMENTARY REPORT

1 Feb 1964

Advanced Fabrication Techniques Branch
Manufacturing Technology Division
Air Force Materials Laboratory
Wright-Patterson Air Force Base, Ohio

AFML Project No. 8-250

(Prepared under The Ohio State University Research Foundation, Intermittent Research Analysis, Contract AF 33(657)-8741
by Chemical and Metallurgical Research, Inc., Chattanooga, Tennessee; Julian Glasser and William E. Few, authors.)

58

FOREWORD

This Final Technical Documentary Report covers all work performed under Ohio State University Research Foundation, Intermittent Research Analysis Contract AF 33(657)-8741, Research Foundation Project No. 1473, by Chemical and Metallurgical Research, Inc. from 27 June 1963 to 30 October, 1963. The manuscript was released 23 January 1964 for publication as an AFML Technical Documentary Report.

This contract with Chemical and Metallurgical Research, Inc., Chattanooga, Tennessee, was initiated under Manufacturing Methods Project 8-250. It was accomplished under the technical direction of Mr. John O. Snyder of the Manufacturing Technology Division, Air Force Materials Laboratory (MATF), Wright-Patterson Air Force Base, Ohio.

Dr. Julian Glasser and Mr. William E. Few of Chemical and Metallurgical Research, Inc. compiled this report from contacts with individuals knowledgeable in the area of joining and allied disciplines.

This project has been accomplished as a part of the Air Force Manufacturing Methods Program. The primary objective of the Air Force Manufacturing Methods Program is to develop on a timely basis manufacturing processes, techniques, and equipment for use in economical production of USAF materials and components. This program encompasses the following technical areas:

- Rolled Sheet, Forgings, Extrusions, Castings, Fiber, and Powder Metallurgy
- Component Fabrication, Joining, Forming, and Materials Removal
- Fuels, Lubricants, Ceramics, Graphites, and Nonmetallic Structural Materials
- Solid State Devices, Passive Devices, and Thermionic Devices

Your comments are solicited on the potential utilization of the information contained herein as applied to your present or future production programs. Suggestions concerning additional Manufacturing Methods development required on this or other subjects will be appreciated.

ABSTRACT
Final Technical Documentary Report

~~ML-TDR-64-35~~
1 Feb 1964

STUDY OF LOW MELT BRAZING ALLOYS

Julian Glasser and William E. Few
Chemical and Metallurgical Research, Inc.

This study brings forth the possibilities of many material compositions which offer potential as low melt braze alloys for joining thin stainless steel strips at temperatures below 1000°F, and with shear lap joint strengths of at least 10,000 psi up to 200°F.

Low melt brazing alloys might find application in such processes involving strip overlap and continuous braze where post heat treating and inert atmospheres may not be practical.

....

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE DIRECTOR:

Melvin E Fields
Col. M. E. Fields
Chief
Manufacturing Technology Division
Air Force Materials Laboratory

TABLE OF CONTENTS

LIST OF TABLES

INTRODUCTION

The objective of the study and analysis described in this report is to provide information which will be helpful in Air Force programs for manufacturing of large rocket motor cases. More specifically, the survey and study was directed to the field of low melt brazing alloys and their applications to joining thin stainless steel strips in a continuous manner with a spiral overlap, which is commonly referred to as "strip-lap" method. The study was directed by Hq. Air Force Systems Command, Air Force Materials Laboratory, Manufacturing Technology Division, to assure having all pertinent data and evaluations concerned with their current and projected programs on fabrication of rocket motor cases.

It is well known that, in the field of joining, soldering technology covers the range of temperatures up to 600 °F. Brazing, on the other hand, starts at about 1000 °F. Therefore, it is evident that there is a "no man's land" for temperatures of joining (soldering or brazing) between 600 °F and 1000 °F. For some applications, this temperature range for brazing might be very important because of the need to have high strength joints at somewhat elevated temperatures, thus eliminating the low melt solders, and the need to join metals at temperatures below 1000 °F in order to avoid heat treating metal parts with subsequent loss of strength. This intermediary range of joining temperature is apparently desired or even vital for the successful development of the strip-lap method for rocket motor case fabrication.

In the strip-lap method for rocket motor case fabrication, stainless steel AM-355, composition 15.50%Cr-4.50Ni-2.85Mo-0.75Mn-0.35Si-0.13C-0.10N-remainder Fe, is used in the form of 4 to 11 mil thicknesses and 1" to 4" wide strip (continuous). This high strength steel has a 350,000 psi tensile as-cold-rolled and after full heat treatment.

Programs are now underway for making up experimental cases 8" diameter by 24" long, starting with about 240 feet of 4 mil thick by 1" wide strip and performing a spiral overlap (80% overlap) with continuous braze. This operation is designed to be performed in the open atmosphere, without any post-heat treatment, and fluxes must be used as needed to assure good bonding. In the spiral overlap technique, very high wrap-around stresses are employed during the fabrication. After it has been fully demonstrated that 8" diameter cases could be constructed or fabricated by the strip-lap method, larger cases would then be fabricated. These would include cases with the following diameters: 39", 65" (Minuteman), 120" (Titan), 150", and 260" (Nova). For these larger cases it is expected that about 11 mil thickness by 4" wide continuous strip AM-355 steel would be used.

The rocket motor cases in question would have service ranges of -60 °F to 200 °F. Also, their hydroburst strength must be very high for this

temperature range. For the required strength the bonding process must result in no less than 10,000 psi tensile shear at the lap joint. To avoid heat treatment and technical difficulties in the spiral overlap technique, the brazing technique should be performed at a temperature below 1000 ^{o}F and this, in turn, would require a braze alloy with a melting range (liquidus-solidus) of about 700 ^{o}F to 900 ^{o}F.

Although studies have been and are probably currently active in the identification, characterization, and use of low melt brazing alloys for the above application, the programs are based, principally, on available information from suppliers of braze alloys. The study and analysis described in this report emphasizes information based on experiences in allied disciplines and also on brazing applications and systems which may not be generally recognized. For example, the information and experiences available in allied disciplines such as the electronic device field, the automotive field, and the dental amalgam field were explored with the revelation of some very interesting prospects and ideas.

This report identifies and characterizes a series of braze alloys which come close to meeting the requirements outlined above. Also, it discusses the application of these low melt braze alloys, as well as their potential to the strip-lap method for fabrication of rocket motor cases. In the course of carrying out the survey and study, many contacts were made with those knowledgeable in the field, particularly in the allied disciplines mentioned, and these contacts are documented in the Contact Reports in Appendix 1.

SUMMARY

The survey and study, on which this report is based, identified and characterized 84 different compositions which offer potential as low melt brazing alloys for joining thin stainless steel strips at temperatures below 1000 °F, and with shear lap joint strengths of at least 10,000 psi at 200 °F. Each of these alloy compositions was first characterized by status of development, being either theoretical, experimental, semicommercial, or commercial. Next, it was characterized by melting range as determined by its actual or estimated phase diagram with the solidus being on the low side and the liquidus on the high side. Next, the probable brazing range was either estimated or determined and, finally, the mechanical properties, particularly shear strength, were determined or estimated wherever possible.

As can be expected, most of the alloys identified are in the experimental stages. One of the problems is in obtaining reliable or any strength data. Either strength data were not available or there was some question as to reliability, accuracy, or meaningfulness. Wherever there was a significant program on determining shear strengths of braze alloys, the test specimens seemed to fail at the interface of the joints and not in the body of the braze alloy material. This indicates that the braze alloy might have strengths meeting the requirements of 10,000 psi shear; however, this was not, in most cases, apparent or obvious from the data obtained in the tests.

Although there is considerable activity or interest in allied disciplines, including the automotive field, the electronic device field, and the dental amalgam field, no specific technology of joining, using low melt brazing alloys, was uncovered which could be used directly for the strip-lap method in question. However, many new ideas and approaches were obtained from these allied disciplines which could form the basis for experimental programs to develop the proper low melt braze alloys and their applications.

Information obtained from the automotive field was somewhat disappointing, and it is suspected that much of the information developed in this industry is proprietary and not being fully revealed. The electronic device field organizations are, of course, very active in joining problems for reasons other than to obtain strong and reliable structures. Their interest is in joining to obtain electromagnetic integrity of devices and components. For example, their principal concern is to have a joint with very good electrical conductivity. One of the items of technology that could be borrowed from the electronic device field is their ability to measure the soundness of a joint, particularly across the interface. Since this seems to be a serious problem for mechanical or structural parts, it appears that this approach, namely, using electronic device test methods, could be profitably used either in in-process inspection or post-process inspection. Furthermore, with somewhat more sophistication, it is probable that the techniques of electronic

test measurements could be used for adaptive controls and in servomechanisms connected with joining problems or equipment.

One of the most interesting types of compositions uncovered in this survey and study was the dental amalgam type alloys. For example, it appears possible to make up an alloy composition containing gallium with a melting point at about room temperature. Such alloys could be made up to melt at a temperature of about 80 °F when the components such as copper, tin, and gallium are mixed as powders. However, these alloys form intermetallic compounds which melt at much higher temperatures, but it takes some time for the reactions to take place to form these intermetallic compounds. Thus, it appears practical to apply an alloy as a paste, at almost room temperature, and let the system set for a matter of an hour to 24 hours to allow the intermetallic compound to set up to a strong solid state. Furthermore, gallium is known for its very high wettability and it may be possible to braze or continuously braze such metals as stainless steel or aluminum at room temperature without the use of fluxes.

Probably the most serious problem in joining high strength stainless steel of thin gauge, using the strip-lap method, is one of fluxing. It is vital to have clean surfaces for continuous braze, and this is not easy when using stainless steel which is well known to form passive (oxide) type surface films. It might be advantageous to employ inert gas atmospheres applied in the form of jets or streams, borrowing the technology used in TIG and MIG automatic welding. Also, the approach of precoating stainless steel strip with the braze alloy, before going to the continuous brazing, appears potentially attractive.

IDENTIFICATION AND CHARACTERIZATION OF BRAZE ALLOYS

A total of 84 compositions have been identified as potential braze alloy systems which might possibly meet the requirements for brazing thin stainless steel by the spiral overlap and continuous braze technique, known as the strip-lap method. Only those alloy systems were selected which offer the possibility of use in brazing at temperatures under 1000 °F.

As can be expected, most of the alloys called out in interviews or uncovered in the literature are either theoretical or experimental types and, therefore, it was not possible to completely characterize most of the compositions. However, it was certainly possible to characterize the compositions as to their status of development, either being theoretical, experimental, semicommercial, or commercial. Also, in most cases it was practical to set a liquidus and a solidus point, and to estimate a brazing range.

Since one of the criteria for an adequate braze alloy is to have a minimum of 10,000 psi tensile shear lap joint strength at a temperature range of -60 °F to 200 °F, all the strength data possible were either collected or estimated. However, this proved to be one of the most uncertain areas in the survey and study because strength data either were not available or were questionable.

The question of fluxes was not ascertained in any detail because this deserves a completely separate treatment. It was felt that the identification and characterization of the alloy compositions should be considered separately, and the following tables present the identification and characterization of these alloys without consideration of fluxing or even the type of metals to be joined. However, characterization of strength is considerably dependent on how the brazing technique was carried out, particularly with respect to controlled atmospheres and/or fluxes. Even though data are shown in the tables for strength, both tensile and shear, much of this is to be questioned as to reliability or accuracy because of the problem of joint failure, not in the braze alloy per se, but at the interface where the braze alloy comes in contact with the parent metal surface or the tinned or coated surface.

The low melt brazing alloys, identified and characterized, are listed in eight tables in accordance with compositions, mainly, silver-base, cadmium-base, tin- and/or lead-base, zinc-base, gold-base, aluminum-base, copper-base, and miscellaneous braze alloys. All those in a specific category, for example, silver-base, contain a minimum of 50% of the base alloy. Or, if there are a multitude of elements present and none are in the majority, the one with the highest composition (plurality) is considered the base element.

Silver-Base Braze Alloys

Table 1 shows 17 compositions of silver-base braze alloys. However, as can be noted from the table, only 4 are identified with quantitative compositions, and the remainder are qualitative compositions. Also included in the tabulation is one exothermic alloy with a composition of 59Ag-41Cu.

The silver-base braze alloys should be considered potentially important because of the extensive use of silver type solder or silver braze alloys in joining stainless steel at temperatures much beyond 1000 °F. For example, the silver-base braze alloys of higher melting points than shown in Table 1 are now being used commercially for bonding stainless steel sandwich construction. To obtain the silver alloys of lower melting range requires, of course, setting up a composition where the melting point of the silver is considerably depressed. There seems to be potential in this direction and it seems probable that if the proper melting range of silver-base braze alloys could be developed, its successful application to a technique such as joining thin stainless steel appears very attractive.

Cadmium-Base Braze Alloys

The cadmium-base braze alloys may well be the most promising for the strip-lap method for immediate applications. Table 2 shows 8 compositions of cadmium-base braze alloy meeting the criteria of brazing range and possibly shear strength.

In Table 2 are shown 3 commercial cadmium-base braze alloys and 5 experimental cadmium-base braze alloys. However, one of the experimental alloys is that studied and developed by The Beryllium Corporation specifically for application to the strip-lap method for rocket motor case fabrication. Since a significant amount of experimental work has been done on this type alloy, namely, 83.2Cd-14.3Zn-2.5Ag, it has a considerable head start in this specific application. Evaluations have been made, utilizing this braze alloy for fabricating 8" diameter cases, using 4 mil thick, 1" wide strips of AM-355 stainless steel, which were precoated with the cadmium-base alloy.

Tin- and/or Lead-Base Braze Alloys

There is probably more information available on tin- and/or lead-base braze alloys than any of the others studied in this survey. Table 3 lists 9 such alloys, 6 of which are commercial type. This is by far the highest percentage of commercial type alloys involved in the study.

The tin- and/or lead-base braze alloys could be expected to be fairly well developed because of their applications in soldering. Therefore, the higher melting point solders were identified and characterized as shown in

TABLE 1

SILVER-BASE BRAZE ALLOYS

Braze Alloy Type	Nominal Composition (Wt. %)	Temperature °F Melting Range Solidus	Liquidus	Brazing Range	Shear Strength (psi)[1]	References[2]
Alpha 525	45Ag-38Au-17Ge	950	995	n. d.[3]	n. d.	15
Dental Alloy	70Ag-25Cu-5Pd	800	850	n. d.	n. d.	9
Experimental	56Ag-44Sb	n. d.	905	n. d.	n. d.	1, 12, 14
Experimental (Exothermic)[4]	59Ag-41Cu	n. a.[5]	n. a.	1000	10,000	12
Theoretical[6]	Ag-Pr					13
"	Ag-Cu					7
"	Ag-Cu-Li					7, 8
"	Ag-Li-Be					7, 8
"	Ag-Li-Pd					7, 8
"	Ag-Cu-Li-Be					7, 8
"	Ag-Cu-Li-Pd					7, 8
"	Ag-Cu-Li-Co					7, 8
"	Ag-Cu-Li-Ni					7, 8
"	Ag-Cu-Li-Be-Pd					7, 8
"	Ag-Cu-Cd-In					7
"	Ag-Cu-Zn-In					7
"	Ag-Cu-In-Sn					7

(1) At 200 F.

(2) References are Contact Report Nos. (see appendix).

(3) n. d. - Not determined (either not tested or data not available).

(4) Nominal composition is ratio of Ag/Cu after exothermic reaction.

(5) n. a. - Not applicable.

(6) Theoretical alloys proposed. Major component is silver with more than 60% Ag.

TABLE 2

CADMIUM-BASE BRAZE ALLOYS

Braze Alloy Type	Nominal Composition (Wt. %) Cd	Zn	Ag	Sn	Be	Temperature °F Melting Range Solidus	Liquidus	Brazing Range	Strength (psi)[1] Tensile	Shear	References[2]
TEC-Z[3]	78.4	16.6	5			n. d. [4]	600	600-800	n. d.	5,000	1, 3, 10
TEC[3]	95		5			64[illegible]	750	800-1000	16,000	n. d.	5, 12, 9
Eutec Rod 155[5]	94		5	1		n. d.	735	750-950	n. d.	n. d.	1
Experimental[6]	83.2	14.3	2.5			n. d.	n. d.	700-900	n. d.	n. d.	3, 5
Experimental	88.3	6.6	5		0.1	n. d.	n. d.	800-1000	n. d.	10,000	3, 5
Experimental	88.4	6.6	5			n. d.	n. d.	800-1000	n. d.	10,000	3, 5
Experimental	93.3	1.6	5		0.1	n. d.	n. d.	800-1000	n. d.	10,000	3, 5
Experimental	94.9		5		0.1	n. d.	n. d.	800-1000	n. d.	10,000	3, 5

(1) At ambient temperature.

(2) References are Contact Report Nos. (see appendix).

(3) Handy and Harman designation (commercially available).

(4) n. d. - Not determined (either not tested or data not available).

(5) Produced by Eutectic Welding Alloys Corporation, Flushing, N. Y.

(6) Preferred alloy developed by The Beryllium Corporation for strip-lap method.

TABLE 3

TIN- AND/OR LEAD-BASE BRAZE ALLOYS

Braze Alloy	Nominal Composition (Wt. %)							Temperature °F			Strength (psi)[1]		Refer-
								Melting Range		Brazing			
Type	Sn	Pb	Ag	Cu	Bi	Sb	Zn	Solidus	Liquidus	Range	Tensile	Shear	ences[2]
Commercial[3]	75		20	3			2	n. d.[4]	750	800-1000	n. d.	n. d.	1
Eutec Rod 157	96.5		3.5					n. d.	430	450-600	5,000	n. d.	12
Eutec Rod 158	40	60						361	455	500-700	14,700	4,500	10, 12
Eutec Rod 153	97.5	2.5						n. d.	579	700-800	10,000	n. d.	12
Commercial	95					5		452	464	500-700	14,000	7,000[5]	12
Commercial		95	5					n. d.	n. d.	n. d.	n. d.	n. d.	8
Semicommercial	90				10			n. d.	600	600-800	10,400	3,000	10, 12
Experimental	95		4			1		n. d.	460	500-700	n. d.	n. d.	9
Experimental	90			10				n. d.	825	850-1000	n. d.	n. d.	9

(1) Lap shear strength and tensile at ambient temperature.

(2) References are Contact Report Nos. (see appendix).

(3) Listed in Kohl, W. H., Materials Technology for Electron Tubes, Reinhold Publishing Co., New York (1951).

(4) n. d. - Not determined.

(5) At 200 F.

Table 3. However, as can be seen in Table 3, they don't all meet the criteria of having a sufficiently high melting point and also, because of this, their shear strengths fall short of the required 10,000 psi. Nevertheless, these alloys are listed and characterized because of the uncertainty or questionableness of the strength data. Because of knowledgeability on these type alloys, they certainly should not be overlooked in any joining problem and specifically for joining at temperatures below 1000 °F.

Zinc-Base Braze Alloys

In Table 4 are listed 12 compositions of zinc-base braze alloys which might meet the criteria of a low melt brazing alloy for application to the strip-lap method using thin stainless steel. Of these 12 alloy compositions, only one is commercial and 2 are semicommercial. The remainder are all experimental; that is to say, some work has been done with them but they have not been applied on a commercial basis. As can be seen from the information shown in Table 4, the liquidus point for most of the alloy compositions is on the low side. Also, shear strength information is essentially nil. As in the case of the tin-base braze alloys, the zinc-base alloys deserve consideration because of their familiarity as solders. Obviously, if the strength of the solders could be increased by increasing their melting points, they might find applications to mechanical structures such as rocket motor cases.

Gold-Base Braze Alloys

The gold-base braze alloys offer some very interesting potentials since they and copper are probably the two best candidate base materials for dental amalgam type alloys. The use of gold for the strip-lap method in fabrication of rocket motor cases may not be prohibitively expensive, since it is expected that less than a few percent of the weight of the structure would be the braze alloy, itself.

In Table 5 are listed 13 different gold-base alloy compositions. Of these, 3 are commercial or semicommercial and the remainder are either experimental or theoretical. Also included in Table 5 are gold-base alloy compositions which could be considered as dental alloys.

For the 3 semicommercial or commercial alloys shown in Table 5, no data are available on shear strength. However, they meet the criteria of brazing temperature range and it might be worthwhile to determine the mechanical properties of these braze alloys at temperatures between -60 °F and 200 °F.

TABLE 4

ZINC-BASE BRAZE ALLOYS

Braze Alloy Type	Nominal Composition (Wt. %) Zn	Al	Fe	Ag	Cu	Mg	Sn	Temperature °F Melting Range Solidus	Liquidus	Brazing Range	Shear Strength (psi)[1]	References[2]
Solder for Al[3]	95	5						720	720	750-900	n. d.	9
Semicommercial	95				5			n. d.	932	950-1050	n. d.	9
Semicommercial	98				2			n. d.	790	800-1000	n. d.	9
Experimental	52					48		n. d.	650	700-800	n. d.	9
Experimental	91.3	5.3	2.4		.08	.02		n. d.[4]	n. d.	700-900	10,000	3, 5
Experimental	61.5	28.6		9.7 (.02Si)				n. d.	885	900-1000	n. d.	3, 5
Experimental	53.1	36.2		4.4 (1Pb-.3Si)			5	n. d.	986	1000-1100	n. d.	3, 5
Experimental	87.5	4.5			2.2		5.8	n. d.	640	650-800	n. d.	3, 5
Experimental	99.1			0.9				n. d.	752	800-1000	n. d.	3, 5
Experimental	99.4		.53		.06			n. d.	700	750-900	5,300	3, 5
Experimental	91.3	5.4	2.4		.79	.17		n. d.	650	700-900	n. d.	3, 5
Experimental	90.5	5.1	4.3		.09			n. d.	708	750-900	n. d.	3, 5

(1) Lap shear strength at ambient temperature.

(2) References are Contact Report Nos. (see appendix).

(3) Listed in Machine Design, September 19, 1963, p. 72.

(4) n. d. - Not determined.

TABLE 5

GOLD-BASE BRAZE ALLOYS

Braze Alloy Type	Nominal Composition (Wt. %)	Temperature °F: Melting Range Solidus	Temperature °F: Melting Range Liquidus	Temperature °F: Brazing Range	Max. Useful Temp. in Air (°F)[1]	References[2]
Semicommercial	73Au-27In	n. d.[3]	840	850-1000	n. d.	1, 12, 14, 15
Semicommercial	94Au-6Si	n. d.	707	750-900	n. d.	1, 12, 13, 14, 15
Dental Alloy	41Au-Cu-Ag	n. d.	850	900-1000	n. d.	9
Experimental	88Au-12Ge	n. d.	673	700-900	n. d.	1, 12, 13, 14, 15
Experimental	80Au-19Sn-1Sb	527	532	550-750	n. d.	12, 13, 14, 15
Experimental	80Au-20Sn	n. d.	536	550-750	n. d.	12, 13, 14, 15
Experimental	75Au-25Sb	n. d.	680	700-900	n. d.	12, 13, 14, 15
Experimental Dental[4]	82Au-18Ga	n. a.[5]	n. a.	80-150	850	12, 13
Experimental Dental[4]	66Au-34Ga	n. a.	n. a.	80-150	1000	12, 13
Experimental Dental[4]	59Au-41Ga	n. a.	n. a.	80-150	900	12, 13
Experimental Dental[4]	33Au-33Ga-33Cu	n. a.	n. a.	80-150	1200	12, 13
Experimental Dental[4]	49Au-30Ga-21Ag	n. a.	n. a.	80-150	900	12, 13
Theoretical	Au-Te	n. d.	n. d.	n. d.	n. d.	13

(1) Temperature where significant strength or negligible flow is retained.

(2) References are Contact Report Nos. (see appendix).

(3) n. d. - Not determined.

(4) Described in National Bureau of Standards Technical Note 140--PB 161641 (April 1962).

(5) n. a. - Not applicable.

Instead of showing tensile or shear strength data for the gold-base braze alloys, there is a column in Table 5 entitled "maximum useful temperature in air." The reason for selecting this type tabulation is that most of the dental amalgam type alloys are characterized in this manner. For example, if a dental alloy has a maximum useful temperature in air at, say, 1000 °F, it means that it has good mechanical properties at this temperature and might well have the minimum required lap shear strength at 200 °F. There are many dental amalgam type alloys, gold-base and particularly those containing gallium, which can be used at very low temperatures, and end up with maximum useful temperatures exceeding 1000 °F. Table 5 shows only a few of these possible compositions, but many more are available.

The potential possibilities of dental amalgam alloys as braze materials for structural applications appears very exciting. The presence of gallium enhances the wettability of any alloy since it is well known that gallium will react with most any metal or oxide composition. Therefore, the flux problem might well disappear if a dental amalgam alloy containing gallium were employed. Gallium is available as a by-product of bauxite which is the basic ore for the production of aluminum metal. However, it is not being recovered because of its lack of saleability. If a low melt braze alloy containing gallium were needed, there would appear to be no difficulty in obtaining adequate quantities at a reasonable price.

Aluminum-Base Braze Alloys

In Table 6 are shown 3 compositions of aluminum-base alloys which offer promise for low melt braze alloys to join thin stainless steel by the strip-lap method. Only one is commercial and this is now being used for brazing aluminum alloy sheet. The aluminum-base braze alloys are interesting and should be further explored because of the experience in brazing aluminum.

Copper-Base Braze Alloys

In Table 7 are shown 5 alloy compositions of copper-base which were identified as potential low melt brazing alloys for application to joining thin stainless steel by the strip-lap method. Of these 5 alloys, only one is commercial, 3 are experimental, and one is theoretical.

As in the case of the gold-base alloys, some of the copper-base alloys shown in Table 7 are dental amalgam types. These all contain gallium and represent only a few of the many compositions of dental amalgam type alloys. The same remarks that were presented for the gold-base dental amalgam type alloys containing gallium could apply as well to the copper-base alloys containing gallium. Copper-base alloys, on the other hand, offer

TABLE 6

ALUMINUM-BASE BRAZE ALLOYS

Braze Alloys Type	Nominal Composition (Wt. %) Al	Si	Ag	Zn	Cd	Temperature °F Melting Range Solidus	Liquidus	Brazing Range	Shear Strength (psi)[1]	References[2]
BAlSi-5[3]	90	10	-	-	-	1070	1095	1090-1120	n. d.[4]	3, 4, 5
Experimental	92.3	.4	5.6	-	1.7	n. d.	940	n. d.	n. d.	3, 5
Experimental	53	.7	3.2	43.1	-	n. d.	960	n. d.	n. d.	3, 5

(1) At ambient temperature.
(2) References are Contact Report Nos. (see Appendix).
(3) AWS-ASTM (American Welding Society--American Society of Testing Materials) Classification. Commercial braze filler metal for aluminum alloy sheet (see reference No. 1 in Appendix 2).
(4) n. d. - Not determined.

TABLE 7

COPPER-BASE BRAZE ALLOYS

Braze Alloy Type	Nominal Composition (Wt. %)	Temperature °F Melting Range Solidus	Liquidus	Brazing Range	Max. Useful Temp. in Air (°F)[1]	Tensile Strength (psi)[2]	References[3]
Commercial[4]	88Cu-4P-8(Sn+Sb)	n. d.[5]	1050	1000-1200	n. d.	80,000	11
Experimental Dental[6]	44Cu-24Sn-32Ga	n. a.[7]	n. a.	80-150	1200	n. d.	12, 13
Experimental Dental[6]	50Cu-18Sn-32Ga	n. a.	n. a.	80-150	1300	n. d.	12, 13
Experimental Dental[6]	66Cu-44Ga	n. a.	n. a.	80-150	1750	n. d.	12, 13
Theoretical	Cu-Ag-Au-(rare earth metals)	n. d	n. d.	n. d.	n. d.	n. d.	13

(1) Temperature where significant strength or negligible flow is retained.
(2) At Ambient temperature.
(3) References are Contact Report Nos. (see Appendix).
(4) Macaloy "F".
(5) n. d. - Not determined.
(6) Described in National Bureau of Standards Technical Note 140--PB 161641 (April 1962).
(7) n. a. - Not applicable (mixture of liquid and powder).

additional interesting prospects because of its lower cost than gold and the potential of higher strength materials.

One approach that could be possibly employed for strengthening copper-base materials is through dispersion strengthening where considerable work has been done by investigators in fields other than brazing alloys. For example, thin strips of copper have been strengthened considerably by internal oxidation of the copper-aluminum type alloy, wherein the aluminum is oxidized, the insoluble oxide providing a dispersoid for strengthening the copper-base material.

Because of promising potential avenues, the copper alloys containing gallium should not be overlooked. If a dental type alloy could be developed such as that of a 66Cu-44Ga composition and applied at temperatures under 150 °F, with a resulting braze alloy system useable up to 1750 °F, joined parts may well be available which are unique and superior to that made by any other method.

Miscellaneous Braze Alloys

Where an alloy composition, which was identified in the survey, could not fit into one of the base metal classifications previously discussed, it was classified as a miscellaneous braze alloy. Table 8 shows 7 compositions of these miscellaneous braze alloys. All the alloys listed in Table 8 are either experimental or theoretical.

The indium type alloys appear interesting because of the well known wettability of indium for oxide type materials. Where a continuous braze is performed at high temperatures on stainless steel, such a wettability might be of utmost importance to alleviate the flux problem or the need for controlled atmospheres. In addition to the indium alloys, the experimental dental amalgam alloys rich in gallium, as shown in Table 8, might also be very interesting because of the extremely low brazing range temperature.

APPLICATIONS OF LOW MELT BRAZE ALLOYS

In the preceding section, the discussion was limited to the identification and characterization of braze alloys without specific consideration to applications such as the materials to be joined, the use of fluxes, the need for inert atmospheres, and the availability and forms of braze alloys. The following will present a generalized treatment of these subjects without specifically considering the strip-lap method, which is considered in the following section of this report.

TABLE 8

MISCELLANEOUS BRAZE ALLOYS

Braze Alloy Type	Nominal Composition (Wt. %)	Temperature °F Melting Range Solidus	Liquidus	Brazing Range	References [1]
Experimental	53Ge-47Al	n. d. [2]	795	850-1000	1, 12, 13, 14, 15
Experimental[3]	57Ca-43Zn	n. d.	782	800-900	9
Experimental	66Bi-34Pd	752	932	950-1050	13
Experimental Dental	Ga-Au-(8-10% Sn)	n. a. [4]	n. a.	50	12, 13
Theoretical	Pr-Ag	n. d.	n. d.	n. d.	13
Theoretical	Pr-Cu	n. d.	n. d.	n. d.	13
Theoretical	In alloys[5]	n. d.	n. d.	n. d.	13

(1) References are Contact Report Nos. (see Appendix).

(2) n. d. - Not determined.

(3) Tend to be explosive.

(4) n. a. - Not applicable (age-hardening alloys).

(5) Indium alloys are available commercially as solders with liquidus temperatures up to 600 F; for higher melting points (to obtain high shear strength of braze at 200 F), new alloys need to be developed.

Type of Materials to Be Joined

Braze alloy compositions and techniques for using these braze alloys are recorded in the literature for joining the popular type alloys, including aluminum, magnesium, copper, carbon and low alloy steels, cast iron, stainless steels, nickel alloys, and tool steels. Also, some knowledgeability is available for joining titanium alloys, beryllium, zirconium, and vanadium alloys, and refractory metals such as tungsten, molybdenum, tantalum, and columbium, etc. Not only is information available for brazing or joining these metals to each other but also some information is available for brazing them to other metals.

For the material in question, namely, AM-355 stainless steel, which consists of 15.5Cr-4.5Ni-2.85Mo-0.75Mn-0.35Si-0.13C-0.10N-remainder Fe, and which is a precipitation hardened or pH type steel, it is necessary that a good bond be obtained in using any braze alloy. It is inconceivable for the brazing temperatures required, namely, under 1000 $^{\circ}$F, that excessive reaction or diffusion of the braze alloys into the parent metal could occur, so this does not present a serious problem. However, the problem of joining this type steel in only 4 mil thickness (up to 11 mil) in strips 1" to 4" wide, by the strip-lap method or continuous braze in the open atmosphere, presents the very serious problem of obtaining a good bond between the braze alloy and the parent metal. If brazing could be successfully performed at temperatures under 1000 $^{\circ}$F, there is no question that the high strength at 350,000 psi tensile of the AM-355 type steel would be retained and no post-heat-treatment processing would be required.

The Use of Fluxes

In all attempts to braze thin stainless steel by the strip-lap method, halide type fluxes have been employed, wherein either the stainless steel was first coated with the braze alloy, or the braze alloy was fed directly to the continuous braze system in the form of foil.

The most promising approach is to use whatever fluxes are needed in precoating the thin stainless steel with about, say, 1/2 mil of desired braze alloy. It is known that halide type fluxes, which consist of halides of sodium, potassium, and lithium, can be used successfully with the stainless steel type of materials, but they would present a problem if they were used during the spiral overlap-continuous braze. However, even though an adequate coating of the braze alloy is placed on the stainless steel strip, there is still a fluxing problem with respect to bonding the coated braze alloy to itself. But this fluxing problem may not be so serious as attempting to flux and braze in one operation. For example, once a coating is obtained, it is not a question of using fluxes which are capable of dissolving the passive coating on stainless steel but one of dissolving and keeping clean the surface of the braze alloy itself.

The Use of Inert Atmospheres

The use of fluxes is, at best, a messy and uncertain operation for the continuous braze strip-lap method. Certainly, if fluxes could be avoided, or used in a minimal manner, the strip-lap method for joining stainless steel has more opportunity for success.

One approach in either supplementing or assisting the fluxing problem is the use of inert atmospheres. For some brazing operations, inert atmospheres are used liberally, particularly for furnacing brazing. In the case of the strip-lap method, it would be necessary to devise a dynamic scheme for keeping the joint under an inert atmosphere at the time the braze is taking place. It appears practical to devise a scheme for doing this, and much of the technology developed in TIG (tungsten inert gas) and MIG (metal inert gas) automated welding could be utilized. As a starting point for the experimental phases, only the best inert atmospheres (helium or argon) should be employed.

Availability and Forms of Braze Alloys

It is expected that a braze alloy could be eventually put into any form needed. For example if foil is required, it would be necessary to make up alloy compositions and roll out the thin foil. If powder is required, powder metallurgy technology for preparing these powders would be used. On the other hand, if a coating of the braze alloy is to be put on the stainless steel before brazing, then most any form of the braze alloy would be adequate as a feed to the melting unit which is used for coating purposes. However, the availability of specific forms of braze alloys with respect to timing for specific applications might be very important. For example, if thin foil is required, it would be necessary to develop technology for rolling the thin foil, if it is not available commercially. This in turn, requires a development or production type program and the proper form may not be available in time. Therefore, the form of alloy which does not require any new production setup for makeup appears most desirable. It seems that all of the 84 compositions described in the previous section could be made up into a form applicable to brazing thin stainless steel by the strip-lap method.

THE POTENTIAL OF LOW MELT BRAZE ALLOYS FOR USE IN THE STRIP-LAP METHOD FOR FABRICATION OF ROCKET MOTOR CASES

If a continuous braze technique could be developed for joining thin strips of high strength stainless steel by the strip-lap method, then it would be possible to obtain rocket motor cases with unique high strength to weight ratios and potentially low manufacturing costs. By use of low melt braze alloys, it would not be necessary to post-heat treat such rocket motor cases since the original strength of stainless steel, such as AM-355, is completely adequate with a tensile strength of 350,000 psi. This tensile strength should be retained if the continuous braze operation could be performed at temperatures under 1000 °F.

An experimental 8" diameter by 24" long rocket type case is being fabricated and tested, using 4 mil AM-355 stainless steel, 1" wide strip, which was precoated with a cadmium-base braze alloy (see Table 2) with a thickness of about 3/4 mil braze alloy. Following the testing of this type casing, it would be necessary to go up in diameter, for example, to fabricate and test cases with diameters of 39", 65" (Minuteman), 120" (Titan), 150", and 260" (Nova). For these larger cases, up to 11 mil thick AM-355 type stainless steel, 4" wide strip, should be used in the wrap-around technique with 80% overlap and a continuous braze. The wall thickness on such cases would be about .473" and they would be required to stand up under high hydro-burst tests for service ranging from -60 °F to 200 °F.

CONCLUSIONS AND RECOMMENDATIONS

Based on information obtained on the survey, together with the study and analysis of data obtained, several conclusions were reached and discussed in the preceding text of the report. These conclusions and recommendations are summarized and itemized as follows:

1. The fabrication and evaluation of rocket motor cases should be continued, using the cadmium-base type brazing alloy, which should be applied as a coating to the thin AM-355 type stainless steel.

2. The use of inert atmospheres, preferably helium or argon, should be tested and applied immediately to the continuous braze.

3. A program should be set up for more adequate testing of the integrity of bonded joints, particularly with respect to the interface problem. For this purpose, technology as developed in the electronic device field should be adopted.

4. The dental amalgam type alloys should be investigated for their potential in joining stainless steel strips by continuous braze. If such alloys are successfully adapted, it can open up an entirely new regime of joining technology.

5. A well defined and semibasic type research program should be considered for studying and developing the low melt brazing type alloys identified and characterized in this report. Much has yet to be done in establishing complete phase diagrams and mechanical properties of these braze alloys, as well as their applications to specific joining problems.

APPENDIX 1

CONTACT REPORTS

CONTACT REPORT NO. 1

Organization Contacted: Battelle Memorial Institute, Columbus, Ohio

Date of Contact: June 28, 1963

Contacted by: Julian Glasser

Personnel Contacted: R. E. Monroe, Welding Engineer

Organizational Activity: Research and information processing (DMIC)

The visit to Battelle was a follow-up of previous contacts made by the Manufacturing Technology Division with Defense Metals Information Center, Robert M. Evans, Senior Engineer. Mr. Evans contributed his comments in writing on April 12 and again on May 17, 1963, and pertinent extracts from these letters are shown below.

Extract from Letter of April 12, 1963

Temperatures of 700 to 900 F are the range in which soldering becomes brazing. The American Welding Society arbitrarily sets 800 F as the temperature which divides the two processes. There is also a notorious lack of suitable filler metals which melt in this range regardless of whether they are called solders or brazing alloys. This "barren" temperature range has been well recognized for many years. However, sufficient need or incentive has never developed to motivate the research necessary to develop appropriate brazing alloys in this temperature range.

There are a number of metals and alloys available commercially which melt in the desired range. We understand Dorr-Oliver has chosen for possible future use one of the better of these, TEC-Z produced by Handy and Harman. This alloy, however, is typical of those available. Most of them are high in cadmium, zinc, lead, or aluminum, and because of this they present wetting, strength, corrosion, and other problems. A few other alloys are known to have been developed, but they are not commercial, and a concerted investigation would be needed to learn more about them for the application you have outlined.

Extract from Letter of May 17, 1963

I have been asked to expand on my letter to you dated April 12, 1963. In it I mentioned the existence of alloys, other than those that are high in cadmium, zinc, etc., which melt in the range 700-900 F.

In mentioning these, I had two particular alloys in mind. The gold-germanium alloy, 88Au-12Ge and the tin-silver alloy, 75Sn-20Ag-3Cu-2Zn. The germanium alloy has received some attention at Battelle as a solder and a dental alloy. It melts at about 675 F. I have briefly discussed the possible applicability of this alloy to brazing with Dr. R. I. Jaffee at Battelle. It is felt that it might work. Some alteration, such as an addition of an element like silicon, might be necessary to promote wetting of stainless steel. The tin alloy is reported to be commercial. It is listed in Kohl, W. H., Materials Technology for Electron Tubes, Reinhold Publishing Company, New York, 1951. I have been unable to find any information on it, however. It melts at 752 F.

Other alloys which melt in the desired temperature range are:

Alloy	Melting Temp. °F
53Ge-47Al	795
56Ag-44Sb	905
73Au-27In	840
94Au-6Si	700

All of these alloys are brittle. This brittleness might not be important for the application desired, however, for two reasons. First, the joint is so thin that a diffusion treatment should produce a ductile joint. This technique is practiced with some of the very brittle high-temperature brazing alloys. Second, the binary alloys only suggest a starting point. Additions of other elements to promote ductility, wetting, and other desirable properties would be necessary.

Another commercial alloy similar to those covered in ASD Interim Report 7-912(VII), March, 1963, is produced by the Eutectic Welding Alloys Corporation, Flushing, New York. It melts at 735 F, and is called "Eutec Rod 155." The composition is about 94Cd-5Ag-1Sn.

Mr. Monroe did not contribute anything new, over and above what Mr. Evans wrote. However, he was very helpful in working up a list of worthwhile contacts.

CONTACT REPORT NO. 2

Organization Contacted:	Materials Advisory Board, National Academy of Sciences, National Research Council, Washington, D. C.
Date of Contact:	July 9, 1963
Contacted by:	William E. Few
Personnel Contacted:	L. L. Gould, Staff Engineer
Organizational Activity:	Advice on materials to all branches of government

---

Mr. Gould is responsible for most of the welding and joining problems associated with Defense Department programs handled at the Materials Advisory Board. After reviewing the problem at hand, concerned with the Dorr-Oliver strip-lap technique, and laying out the requirements for joining, Mr. Gould suggested the following organizations might well have some background worth looking into. The three organizations suggested, with appropriate personnel to contact, are as follows:

1. Chance Vought Aircraft Company, Dallas, Texas; G. Allen Starr, Chief Engineer, Applied Research and Development; J. A. Millsap, Chief of Manufacturing Research and Development

2. Convair, Fort Worth, Texas; W. O. Sunafrank; W. E. Johnson; D. A. Redwine, Project Coordinator on a titanium program

   Mr. Gould felt that some of the background developed on the fabrication of titanium sandwich structure might be applicable to the program in question.

3. Boeing, Seattle, Washington; John Stacy, Engineering Department; Andrew G. Lucas, Manufacturing Department

CONTACT REPORT NO. 3

Organization Contacted: Dorr-Oliver, Inc., 77 Havemeyer Lane, Stamford, Connecticut

Date of Contact: July 11, 1963

Contacted by: Julian Glasser and William E. Few

Personnel Contacted: Walter Arrowsmith, Program Manager on Air Force Brazing Project

Organizational Activity: Engineering

Dorr-Oliver was contacted early in the survey in order to avoid duplication of effort and to learn the exact status of their project. Apparently, the state-of-the-art survey made in August 1962 covered only suppliers of braze alloys and organizations like Battelle (DMIC) which are chartered for supplying information. The automotive industry, such as General Motors and Ford, and the electronic device industry, such as Bell Laboratories and RCA, were not covered in this past survey.

Mr. Arrowsmith claimed that the reason for directing effort toward utilization of a lower-melting-point braze alloy is because of loss of strength in AM-355 at temperatures above 950 F. It is desirable to retain 98% of the base strength of the cold-rolled strip at room temperature, and this could not be done if brazing were performed at 1100 F. The higher-melting braze alloys used in the past consisted of Ag-Cu-Cd-Zn compositions. The Beryllium Corporation actually made the survey on braze alloys of lower melting points.

The braze alloys with flow temperatures of not more than 1000 F, which were proposed by The Beryllium Corporation, consisted of Al-Si alloys and Cd-Zn-Ag types. The Al-Si braze alloy is typified by the Alcoa braze sheet, consisting of 90Al-10Si. The Cd-Zn-Ag alloy is typified by Handy and Harman's TEC-Z consisting of 78.4Cd-16.6Zn-5Ag. Mr. Arrowsmith reported that a modification of the latter alloy is soon to be tested in the program by making up an 8" diameter casing from 4 mil strip. The braze alloy to be used would contain 83.5Cd-14Zn-2.5Ag, with a flow range of 550-600 F.

The low-melting braze program is now at the stage where The Beryllium Corporation is preparing 240 feet of 4 mil strip, 1" wide, coated with the last-mentioned braze alloy about .00075" thick. Dorr-Oliver would then use this coated strip of AM-355 high-strength steel to make up, by the

strip-lap method, a case 8" diameter by 24", and evaluate its properties. In making up this strip-lap case, the use of halide-type fluxes would be avoided and attempts would be made to use organic fluxes instead.

The contact with Dorr-Oliver was very helpful for orientation, particularly with respect to the effort at The Beryllium Corporation and the activities at Dorr-Oliver.

CONTACT REPORT NO. 4

Organization Contacted: Avco Corporation, Nashville Division, Nashville, Tennessee

Date of Contact: July 26, 1963

Contacted by: Julian Glasser

Personnel Contacted: H. J. Black, Director of Engineering; W. Brandel, Head of Materials Research

Organizational Activity: Metal fabricators (sandwich construction, etc.)

The closest allied technology at Avco/Nashville is their program on brazing aluminum sandwich construction. Although the most popular way of binding aluminum honeycomb is with organic adhesives, there is a serious need for metal brazing because of the deterioration of organic compounds in space and radiation environments. They have made up some sandwich structures, utilizing their techniques for high-strength-steel sandwich structures, with braze alloy material consisting of 90Al-10Si.

It was pointed out that the Dorr-Oliver technique is seriously handicapped because it does not braze in an inert atmosphere and requires brazing simultaneously with wrapping. The overall problem would be simplified if the wrapping could be done first, using a tack-type brazing and then followed up by filling with an aluminum-type braze alloy in an inert atmosphere, using no fluxes. Another approach would be to wrap at room temperature with foils of the brazing alloy in place and with brazing alloys of melting points of 1300 to 1700 F, followed by a braze and heat treat cycle of the entire structure in an inert atmosphere under fluxless conditions. Overall, the use of fluxes is a serious problem, but cannot be avoided if brazing is to be done in the open atmosphere, which is characteristic of the Dorr-Oliver strip-lap method.

Several new contacts were suggested, including North American Aviation, Los Angeles Division, who are brazing AM-355 steel in the B-70 program. Also, the project carried out by Southern Research Institute, on behalf of NASA, on evaluation of solders, was pointed out.

CONTACT REPORT NO. 5

Organization Contacted: The Beryllium Corporation, Reading, Pennsylvania

Date of Contact: August 6, 1963

Contacted by: Julian Glasser

Personnel Contacted: W. H. Santschi, Engineering Manager, Technical Division; E. E. Weismantle, K. C. Taber

Organizational Activity: Production and fabrication of beryllium and allied metals

---

The project at The Beryllium Corporation, which is a subcontract to the Dorr-Oliver project, on braze alloy materials is essentially complete. The program and accomplishments were reviewed in some detail as follows:

The first phase of the program was braze alloy selection. This included studies of fluxes and surface treatments. The overall program of braze alloy selection was originally scheduled for six months, with one month on fluxing materials, one month on effect of surface finish (four types of finishes were evaluated), one month on effect of alloy composition (contact angles on melting were measured), one month on adjustment of composition to achieve optimum alloying, one month of evaluation of joint strengths and malleability and, finally, one month on alloy optimization. In the first four parts of phase 1, cooling curves, metallographic techniques and microtests were used to screen out braze alloys. The actual project for phase 1 was started on December 16, 1962, and completed at the end of July 1963.

Phase 2 of the project is directed to providing braze alloys in foil or as coatings. The original objective was to provide braze alloy materials for five coils, 1" wide and 4 mil thick, for the three most favorable braze alloy systems. Actually, this phase has been modified, with the alloy selection being limited to one composition, namely, the 83.2Cd-14.3Zn-2.5Ag (M. P. 550-660 F). The flux selection is zinc chloride and ammonium chloride in water solution. The form of braze alloy was chosen to be a coating .75 mil thick on AM-355 steel. The surface treatment should be vapor blasted, but the as-cold-rolled condition (Allegheny Ludlum's XH designation) appears almost as good, and this will be used. In this phase 2, one coil of coated strip 700 feet long has already been produced, which is sufficient to make up two 8" diameter test casings. Dorr-Oliver plans to use an organic flux, such as oleic or stearic acid, for this coated strip. At the time of the contact, the people at The Beryllium Corporation were awaiting instructions from Dorr-Oliver as to the next activity on phase 2. This phase for providing braze alloys was originally scheduled for one month.

In The Beryllium Corporation's survey, the only commercial braze alloys found of the proper liquidus-solidus range were Handy and Harman's TEC and TEC-Z. The first is a Cd-Ag alloy, and the second is modified to contain zinc. The addition of zinc depresses the melting point and contributes room temperature strength. The alloy actually selected is a modification of the TEC-Z alloy.

In ASD Interim Report TR-7-912(VII), March, 1963, on the braze alloy selection phase of the program carried out by The Beryllium Corporation, many alloy compositions were identified and described. Tests indicated that five alloys produced shear strengths in excess of 10,000 psi, and compositions (wt. %) of these alloys are as follows:

91.3Zn-5.3Al-2.4Fe-0.8Cu-0.2Mg

88.3Cd-6.6Zn-5.0Ag-0.1Be

88.4Cd-6.6Zn-5.0Ag

93.3Cd-5.0Ag-1.6Zn-0.1Be

94.9Cd-5.0Ag-0.1Be

Although data on melt and flow temperatures were not reported, the alloys listed above were probably selected because they met the requirements of a liquidus-solidus range of 700-900 F.

Other compositions of multiple alloys reported in TR-7-912(VII) are as follows:

Approx. Melting Temp. (°F)	Composition (wt. %)
885	61.5Zn-28.6Al-9.7Ag-0.2Si
960	53Al-43.1Zn-3.2Ag-0.7Si
986	53.1Zn-36.2Al-5Sn-4.4Ag-1Pb-0.3Si
640	87.5Zn-5.8Sn-4.5Al-2.2Cu
752	99.1Zn-0.9Ag
940	92.3Al-5.6Ag-1.7Cd-0.4Si
-	99.4Zn-0.06Fe-0.03Cu
700	99.4Zn-0.53Fe-0.06Cu
650	91.33Zn-5.35Al-2.36Fe-0.79Cu-0.17Mg
708	90.47Zn-5.09Al-4.35Fe-0.09Cu

CONTACT REPORT NO. 6

Organization Contacted: A. O. Smith Corporation, Milwaukee, Wisconsin

Date of Contact: August 6, 1963

Contacted by: William E. Few (telephone contact only, to determine desirability of personal visit)

Personnel Contacted: M. A. Scheil, Director of Metallurgical Research

Organizational Activity: Manufacturing of welding and joining equipment and supplies

---

The telephone contact proved to be sufficient to ascertain that A. O. Smith Corporation has nothing to offer in the way of technology on low temperature brazing or soldering techniques. All of their joining techniques and problems have been associated with the conventional high-temperature brazing alloys. Mr. Scheil did suggest that a contact should be made with Chicago Bridge and Iron, since he felt they might have some technology which would be applicable to the problem. However, in following up on this suggestion, it was learned that the primary experience at Chicago Bridge and Iron is not related or applicable to the low-melting braze alloy for the strip-lap method.

CONTACT REPORT NO. 7

Organization Contacted: IIT Research Institute, Chicago, Illinois

Date Contacted: August 26, 1963

Contacted by: Julian Glasser

Personnel Contacted: J. F. Rudy, Head, Welding Research

Organizational Activity: Research

Although the welding research group at IIT Research Institute does not have any specific experience with braze alloys flowing at 700 to 900 F, they do have some ideas with respect to a development program. This program would involve the investigation of ternary and quaternary systems based on silver. Compositions of systems would include about 60% silver containing copper, lithium, beryllium, palladium, cobalt, nickel, indium, cadmium, zinc, and/or tin. From these components more than 200 alloys could be initially selected, either 2, 3, or 4 at a time. A program could be worked up for six months at a cost of about $25,000 to the stage of obtaining the 10 most promising alloys. To reach this stage, phase diagrams would be evaluated and physical properties, such as melting points and hardness, would be measured in the laboratory for screening purposes.

CONTACT REPORT NO. 8

Organization Contacted: Ford Motor Company, Manufacturing Development Department, Detroit, Michigan

Date of Contact: August 27, 1963

Contacted by: William E. Few

Personnel Contacted: John M. Diebold, Manager, Welding Development; Richard E. Brooks and R. H. Vetter (both work in the Welding Development Department)

Organizational Activity: Develop manufacturing techniques for the Ford Motor Company

---

It does not appear that the Ford Manufacturing Development group has much specific input to make to this project. However, they did have one or two specific comments pertaining to lithium solders. According to some studies they have been concerned with, a solder with .25% to .5% lithium can many times be beneficial, as an addition to all types of solders, since it acts as a good deoxidizer. Mr. Brooks suggested contacting Lithium Corporation of America concerning all types of lithium-containing solders.

Most of the Ford applications are involved with routine high-temperature brazing or the more conventional low-temperature soldering. They have not done, nor do they profess to have any internal requirements which would call for this intermediate temperature range of solders, that is, the 700 to 900 F range.

In searching for information of the type the Air Force is looking for, they did mention specific organizations which they thought might have information useful to the project, as follows:

1. Ferrotherm Corporation, 186 E. 65th St., Cleveland, Ohio: Jack Gier, President

2. Aerobraze, Cleveland, Ohio; Sam Wheland

   (Aerobraze is reported to have a 5% silver-lead solder which, apparently, some of the Ford people feel might be useable in this application.)

The Ford people also suggested contacting a Roger Clark at General Electric Company, One River Road, Schenectady, N. Y., concerning a recent welding innovation developed at General Electric and referred to as "spike welding." They report that this technique has been used quite successfully on stainless casings for igniter type tubes. Other welding techniques, they believe, should be investigated as a means of fabricating the structure in question. Additional suggested contacts would be with Sonobond, Westchester, Pennsylvania, who are concerned, of course, with both ultrasonic welding and also cold welding.

CONTACT REPORT NO. 9

Organization Contacted:	General Motors Technical Center, Manufacturing Development Laboratory, Warren, Michigan
Date of Contact:	August 28, 1963
Contacted by:	William E. Few
Personnel Contacted:	H. D. Hall, Director of Manufacturing Development; R. A. Featherstone, Director of Engineering; A. Katzer, Senior Welding Engineer; H. J. Gilliland, Supervisor of Metallurgy
Organizational Activity:	Development of manufacturing techniques and processes for the General Motors Corporation

---

From this particular group, nothing was learned concerning the reported announcement that General Motors had a method of joining thin stainless steel to low carbon steel. Either this reported development is being done by another group within the General Motors Corporation, which could not be ferreted out, or else this particular manufacturing development group chose not to talk about it.

However, this group is actively involved in looking for brazing and joining compounds directly in the temperature range in question, namely, 700 to 900 F. Their concern is not for joining high-strength steels, and the exact application and materials involved were not determined since, again, they outspokenly did not want to discuss the final endpoint application. However, they did list many alloys which they felt should be looked into if they have not already been evaluated by the Dorr-Oliver or The Beryllium Corporation programs. The alloys suggested are as follows:

1. A 41% Au-Cu-Ag alloy; liquidus of 850 F (dental alloy)

2. A 70% Ag-Cu-Pd alloy which has a 70-25-5 composition and a reported liquidus of 800-850 F

3. A 95% Cd-5% Ag, with a solidus of 640 F and a liquidus of 740 F

4. A 95Zn-5Al alloy, which was discussed in Welding Engineer, September 1957 (and Machine Design, September 19, 1963).

5. A 1% Sb-95% Sn-4% Ag alloy, which has a very low melting point of 450 to 460 F. They did indicate that this alloy might not meet the strength requirements but that this fact should be determined. They report that this composition was developed at Bendix Aviation and, they thought, on an Air Force Contract.

6. In addition to those listed above, they reiterated the following compositions: 95% Zn-5% Cu, liquidus 932 F; 98% Zn-2% Cu, 790 F liquidus; 90% Sn-10% Cu, liquidus 825 F.

7. Two other specific compositions were given which they felt hold promise, but cautioned that their use and application has to be extremely well handled since the alloys, themselves, tend to be explosive. These are as follows: 48% Mg-52% Zn, with a liquidus of 650 F; 57% Ca-43% Zn, with a liquidus of 782 F.

None of the above alloys suggested by the General Motors staff people have been compared with some of those tried on the Dorr-Oliver program.

CONTACT REPORT NO. 10

Organization Contacted: National Aeronautics and Space Administration, Marshall Space Flight Center, Huntsville, Alabama

Date Contacted: September 5 and 6, 1963

Contacted by: Julian Glasser

Personnel Contacted: C. E. Cataldo, Chief, Metallic Materials Branch, Materials Division, Propulsion and Vehicle Engineering Laboratory; S. D. Ebneter, Test and Development Engineer (Chrysler Corporation), Quality and Reliability Assurance Laboratory

Organizational Activity: Monitoring and support of space vehicle programs

---

The metallurgical group at MSFC was contacted because of their project with Southern Research Institute on joining, as reported on March 19, 1962, on contract NAS8-1563. The following are pertinent data extracted from the report titled "Investigation of the Mechanical Properties of Soldered Joints at Very Low and Elevated Temperatures."

Solder	Flow Temperature (°F)	Strength (psi at 70 °F) Tensile	Strength (psi at 70 °F) Shear
Anchor (40Sn-60Pb)	460	10,942	3,758
SRI W4 (90Sn-10Bi)	600	10,425	2,983
H&H TEC-Z (5Ag-16.6Zn-78.4Cd)	600	5,875	4,933

No other projects have been sponsored by MSFC bearing on the brazing problem. For details on the Southern Research project, it was suggested that J. R. Kattus, Metallurgy Division at Southern Research Institute, be contacted.

MSFC has active contracts on adhesive bonding for metals and plastics, such as at Narmco, but these are for cryogenic temperature applications and not pertinent to the brazing problem. Most of the experience of MSFC deals with Niro alloys with compositions such as 82% Au-18% Ni (flow temperatures of 1500-1600 F) or 90% Ag-10% Pd (flow temperatures of 1800-1900 F).

Mr. Ebneter was contacted for the purpose of learning of any experience in joining electronic components. His shop is concerned with joining metal leads which pass through glass encapsulated transistor and diode materials. Materials to be joined are Covar (Ni-Fe-Co), Dumet, and other nickel-copper alloys. However, all these joining techniques involve use of high-temperature silver-type solder with flow temperatures above 1000 F.

CONTACT REPORT NO. 11

Organization Contacted: Ohio State University, Welding Engineering Department, Columbus, Ohio

Date of Contact: September 25, 1963

Contacted by: William E. Few and Julian Glasser

Personnel Contacted: Professor Roy B. McCauley, Head, Welding Engineering Department

Organizational Activity: Welding research and development

Professor McCauley had the following braze alloy to recommend for possible application to the strip-lap methods. This is an alloy developed by McCauley Alloy Company, Steger, Illinois. The owner of this company was Professor McCauley's father who is now deceased. The alloy recommended is a copper-base alloy with approximately 4% phosphorus and 2%-12% combined addition of tin and antimony. The alloy has a melting point of 1050 F, which is a little bit high for the application in question. This particular alloy is referred to as Macaloy "F". It has a tensile of 80,000 psi at room temperature and is somewhat self fluxing and Sn-P provides good wettability. At the present time it is widely distributed by Montgomery and Ward. The alloy requires low-melting fluxes such as a fluoride dissolved in water plus borax-type mixtures.

This particular alloy is reported to be quite workable and has been drawn into very fine wire by National Standards Company of Niles, Michigan. On this particular application, it was used to braze electrical busses. Super-Cut, Inc. used this alloy for setting diamonds in cutting tools and wheels.

Professor McCauley feels that the overall field of brazing has been badly neglected and needs additional fundamental work on interface effects in thicknesses of less than .0005". He believes that the practical aspects of brazing and/or soldering in a structure of the type in question can best be accomplished by keeping the brazing layer between .0003" to .00015". He refers to this range as the practical range of brazing.

One possible suggested lead by Professor McCauley was an organization called Fusion (producers of braze alloy powders) located in Cleveland, Ohio. The man to contact in this organization is Bruce Williams.

CONTACT REPORT NO. 12

Organization Contacted: Tin Research Institute, Columbus, Ohio

Date of Contact: September 26, 1963

Contacted by: William E. Few and Julian Glasser

Personnel Contacted: J. B. Long

Organizational Activity: Promote the useful application of tin and tin-containing materials through a well organized technical service activity

---

After discussion, Mr. Long had the following recommendations to make in regard to possible alloys for joining AM-355 stainless steel strip. The alloys suggested by Mr. Long and the staff at Tin Research Institute are as follows:

Eutec Rod	Alloy Composition	Flow Temp. or Melting Range (^{o}F)	Tensile Strength (psi)
155	95Cd-5Ag	640-750	(16,400 at R. T. (4,400 at 300 F
157	96.5Sn-3.5Ag	430	5,000 at R. T.
158	40Sn-60Pb	361-455	10,000 at R. T.
153	97.5Pb-2.5Ag	579	10,000
	95Sn-5Sb	452-464	
	56Ag-44Sb	905	
	94Au-6Si	707	
	53Ge-47Al	795	
	88Au-12Ge	673	
	73Au-27In	840	
	5Sn-3Cu-92Zn	390-822	15,000 (approx.)
	10Sn-3Cu-87Zn	390-835	
	80Au-19Sn-1Sb	527-532	
	80Au-20Sn	536	
	75Au-25Sb	680	
	90Sn-10Bi	600	

Mr. Long also suggests the possibility of looking at the diffusion bonding techniques for possible application on this joining problem. In particular, he feels the diffusion bonding techniques reported by Niemann at Battelle should be evaluated. Other work thought worthy of consideration is that done by the National Bureau of Standards on gallium-copper, gallium-gold with 8%-10% tin which melts at 50 F and is an age-hardening alloy. He further suggests the possibility of heat treating to the desired properties during brazing. Exothermic brazing was also suggested, with reference to NARMCO and their publication of August 1941 covering Mg-B-Ag_2O type compositions.

Mr. Long pointed out that many of the compositions named in their suggested list are actually fairly brittle or nonductile materials. However, in the application in question, it appears to be the consensus of opinion of many organizations contacted that possibly the base ductility of the brazing compound may not be important at all. An example of the type of alloys in question is the 53Ge-47Al which would be brittle. However, it might serve as a useful brazing alloy in the application in question. Mr. Long believes that the work done at the National Bureau of Standards concerned with gallium alloys could well have application on this solid rocket motor case problem. He has agreed to supply us with additional information concerning a better identification of the NBS work. Some of the alloy compositions shown in the above list, namely, the 95Cd-5Ag, the 94Au-6Si, the 88Au-12Ge, the 75Au-25Sb, all have been suggested by other organizations during the course of this survey and study and therefore probably deserve special mention and consideration.

CONTACT REPORT NO. 13

Organization Contacted: Ohio Semiconductors, Division of Tecumseh Products Company, Columbus, Ohio

Date of Contact: September 25, 1963

Contacted by: William E. Few and Julian Glasser

Personnel Contacted: W. E. Bulman, President; Dr. Arthur E. Middleton, Chief Scientist

Organizational Activity: Manufacture of specialty semiconductor materials and solid state devices

---

The solid state device industry and semiconductor people are constantly plagued with problems in joining, wherein good thermal conductivity and good electrical conductivity are important. Their mode of determining satisfactory bonding is through careful and precise electrical measurement techniques not normally used in the routine metallurgical joining field. Although it has not been proved that a good electrical bond does result in a good mechanical and high strength bond, it is nevertheless assumed that the two are somewhat inseparable. The solid state device people sincerely believe that this is true and could be proved through a carefully controlled experimental program. As previously reported in Contact Report No. 12 (Tin Research Institute), the Ohio Semiconductors personnel also believe that some of the nonductile materials, such as previously described in report No. 12, should be seriously considered. They further believe that the hard gallium solders which melt between 727 F and 1652 F, which were developed by the National Bureau of Standards, should also be seriously evaluated. Some references which they thought worthy of critical review are given at the end of this report.

Dr. Middleton further believes that the gold-tellurium system should be looked at and, in addition, the bismuth-palladium system with 66% bismuth which has a melting point of 752 F to 932 F. Another metal system not previously mentioned by any organizations contacted is the copper-silver-gold plus small additions of rare earths. Praseodymium-silver and praseodymium-copper were two other systems believed to be worthy of consideration. Finally, like other organizations, it is Middleton's belief that even though many intermetallics will be brittle in their own right, nevertheless, they should be investigated as potential joining compounds for the problem at hand since, with a very thin bonding layer, the ductility of the joining material may have no bearing on the overall brittleness of the joint.

Many of the metal systems suggested by Ohio Semiconductors have been worked on by people in the electronic device field, but with a far different application in mind than brazing solid rocket motor cases. Some of the references supplied are given below.

1. An article entitled "Design Criteria for Solders in Cryogenic Environments," by J. L. Christian, General Dynamics/Astronautics, General Dynamics Corp., San Diego, Calif. Published in Electro-Technology magazine, June 1963.

2. "Hard Gallium Alloys for Use as Low Contact Resistance Electrodes and for Bonding Thermocouples into Samples," by George G. Harman, Electron Device Section, National Bureau of Standards, Washington, D. C. In Review of Scientific Instruments, Vol. 31, No. 7, July 1960.

3. "Detailed Techniques for Preparing and Using Hard Gallium Alloys," U. S. Department of Commerce, Office of Technical Services, PB Report 161641, 1962.

4. "Intermediate 'Indalloy' Solders," published by Indium Corp. of America, 1676 Lincoln Ave., Utica 4, N. Y.

CONTACT REPORT NO. 14

Organization Contacted: Radio Corporation of America, Chemical and Physical Laboratory, 415 South Fifth Street, Harrison, New Jersey

Date of Contact: October 9, 1963

Contacted by: William E. Few

Personnel Contacted: Carel W. Horsting, J. J. Carrona, Manager, Chemical and Physical Laboratory

Organizational Activity: Development work concerned with joining and soldering devices in both the electronic tube field and the electronic solid state device area

---

After explaining in some detail the strip-lap method of fabricating solid rocket motor cases, both Mr. Horsting and Mr. Carrona feel that there may be technology within their specific competence which could be applied to this particular project. However, in discussing this, they felt that much of their information was proprietary and they would like time to consider what the RCA position should be on releasing any such information.

Nevertheless, like other electronic device people who have been contacted during the course of this survey and study, they feel that some of the brittle, nonductile materials should be investigated, because ductility in the base joining material may not be important. Specifically, they listed the same alloys as supplied by Ohio Semiconductors as potential candidates, as well as the same list which was supplied by the Tin Research Institute, namely, the alloys containing silver-antimony, gold-silicon, germanium-aluminum, gold-germanium, and possibly gold-indium.

They readily admit that they know very little about the strength of these particular alloy compositions since strength is not a critical criteria in the electronic device application of these materials. Mr. Carrona did suggest that we send them a list of the alloys which have proved most successful thus far and a graphic representation or picture of the type of machine which Dorr-Oliver is using in their manufacturing operation, in order that they might think about possibly submitting detailed ideas for carrying out a short range development program in order to evaluate some of the materials in question. There was an indication that RCA would be interested in undertaking such a laboratory development project as this.

CONTACT REPORT NO. 15

Organization Contacted:	Bell Telephone Laboratories, Murray Hill, New Jersey
Date of Contact:	October 9, 1963
Contacted by:	William E. Few
Personnel Contacted:	Wallace G. Bader, Engineer
Organizational Activity:	Development work associated with problems concerned with joining of solid state devices

---

Basically, the contact with Mr. Bader merely confirms the opinion that some of the nonductile materials used for joining solid state devices should be investigated for this particular application. He suggests exactly the same types of compositions as were suggested by the Tin Research Institute, Ohio Semiconductors, and Radio Corporation of America. Like the others, he can supply no strength data on these particular materials. He did suggest the testing of one commercial alloy supplied by Alpha Metals, Inc., which is a 38% Au-17% Ge-45% Ag. This alloy is commonly referred to as Alpha #525 and it has a melting range of 950-995 F. He believes that either this alloy or some modification of it might be applicable to the particular job of brazing. His suggested contact at Alpha Metals is Fred Disque, Director of Research. Apparently, Alpha Metals produces this material commercially. Mr. Bader also believes that an organization named Alloys Unlimited also can supply this alloy or modifications in commercial quantities.

However, he pointed out that he did not believe it could be supplied in foil of sufficient width for the application in large solid rocket motor cases made by the strip-lap method.

Mr. Bader did point out that he believed this particular brazing problem could be solved by people in the electronic device field, by using their background in the joining of solid state devices. However, there is no immediately available technique that can be readily lifted and applied to this particular problem. He feels, like the others, that it will require some small amount of development work in order to prove feasibility. Bell Laboratories has no interest in undertaking contracts of this type.

APPENDIX 2

LIST OF SELECTED REFERENCES

1. Borcina, David M. "Soldering and Soldering Alloys," in Machine Design (Nonferrous Metals Book Issue), Vol. 35, No. 22, September 19, 1963, pp. 69-74.

2. Brazing Manual, prepared by AWS Committee on Brazing and Soldering. Reinhold Publishing Corp., New York, N. Y., 1963.

3. Card, T. B. "Striplap Method of Rocket Motor Case Fabrication." ASD Interim Reports 7-912(VI), 7-912(VII), and 7-912(VIII), Thiokol Chemical Corp., Wasatch Div. report for Manufacturing Technology Laboratory, ASD, WPAFB, Ohio.

4. Citrin, G. "Evaluation of High-Strength Lightweight Laminated Pressure Vessels of Lap-Joint Construction." Fourth Quarterly Report No. WAL TR 766.2/3-3, by Republic Aviation Corp., Mineola, L. I., N. Y. for Watertown Arsenal, January 16, 1963.

5. Dowd, J. D. "Soldering Aluminum: A Report," in Welding Engineer, p. 43, September, 1957.

6. Harman, George G. "Detailed Techniques for Preparing and Using Hard Gallium Alloys." Technical Note 140, PB 161641, National Bureau of Standards, April, 1962.

7. Indium Corporation of America. "Indalloy Intermediate Solders." Utica, N. Y., 1957.

8. Jaffee, R. I., and Weiss, Marguerite G. "Properties of the Alloys of Indium with Lead, Tin, Bismuth, and Cadmium." Battelle Memorial Institute, Columbus, Ohio, 1954.

9. Pattee, H. E. "Brazing and Brazing Alloys," in Machine Design (Nonferrous Metals Book Issue), September 19, 1963, p. 75.

10. Rudy, John F. "Welding and Welding Alloys," in Machine Design (Nonferrous Metals Book Issue), Vol. 35, No. 22, September 19, 1963, pp. 79-84.

11. Smith, D. L., and Caul, H. J. "Alloys of Gallium with Powdered Metals as Possible Replacement for Dental Amalgam," in the J. of the American Dental Assoc., Vol. 53, pp. 315-324, September, 1956, Chicago, Ill.

12. Smith, D. L., Caul, H. J., and Sweeney, W. T. "Some Physical Properties of Gallium-Copper-Tin Alloys," in the *J. of the American Dental Assoc.*, Vol. 53, pp. 677-685, December, 1956, Chicago, Ill.

13. Troy, W. C. "Development of Low Temperature Brazing Alloys for Titanium Honeycomb Sandwich Materials." ASD TR 61-313, Part II, January, 1963. Report of Solar, a subsidiary of International Harvester Co., San Diego, Calif. for the Directorate of Materials and Processes, ASD, WPAFB, Ohio.

14. "Solders for Use on Aluminium and Zinc," in *Metal Industry*, p. 515, April 11, 1963.

15. Willhelm, A. C., and Hamilton, J. A. "Investigation of the Mechanical Properties of Soldered Joints at Very Low and Elevated Temperatures." Summary Report by Southern Research Institute, Birmingham, Ala. to Marshall Space Flight Center, Huntsville, Ala., March 19, 1962.